

Understanding the Performance of Transition Metal Oxide-Carbon Composite Catalysts in Air Electrodes for Metal-Air Batteries and Alkaline Fuel Cells

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Various kinds of transition metal oxides such as calcium-doped lanthanum cobalt oxide (LCCO), lanthanum calcium cobalt manganese oxides, nickel cobalt oxides are potentially low-cost catalysts for oxygen reduction reaction in metal-air batteries. In our recent studies, we have found that conductive carbon materials added to transition metal oxides such as LCCO increase the electrocatalytic activity of the oxide several times. In this presentation, we discuss the effect of carbon additives on the ORR performance of the oxides.

We have made polarization studies on rotating ring-disk electrodes coated with catalyst layers consisting of various mass ratios of transition metal oxide to carbon, different types of transition metal oxides and different types of carbon additives. The thin film composite catalyst layers were prepared on a glassy carbon electrode and the oxygen reduction activity in 1 M potassium hydroxide was investigated using very slow linear sweep voltammetry (2 to 5 mV/s) between 0.1 V and -0.5 V vs the mercury-mercuric oxide electrode and disk electrode was rotated at 400, 900, 1600 and 2500 rotations per minute (rpm). The production of hydrogen peroxide intermediates during oxygen reduction was followed at the ring electrode held at + 0.5 V for oxidizing the peroxide. The data was analyzed by the standard Koutecky-Levich method to obtain the kinetic parameters.

In most of the previous studies on the use of transition metal oxides as catalysts for the oxygen reduction reaction, these oxides have been mixed with a highly conducting carbon such as acetylene black or graphite. Typically, a mixture consisting of approximately 80% (w/w) oxide and 20% (w/w) of high-surface area carbon is used. The carbon additive is described as necessary to enhance the electrical conductivity of the poorly-conducting transition metal oxide catalyst[1-4]. Further, these studies on "carbon-containing composite catalysts" ascribe the observed variations in catalytic activity for the electro-reduction of oxygen entirely to the properties of the transition metal oxide, and the electrocatalytic activity of carbon is often completely ignored.

We found that high oxygen reduction activity of the carbon-containing composite catalysts comes from a synergistic role of the oxides and carbon additive. We verified that the carbon additive works as primary electrocatalysts for the electro-reduction of oxygen to hydroperoxide. The catalytic activity increased with the amount of carbon (Fig. 1). While the ring current suggested 95% hydroperoxide production on carbon, in the presence of transition metal oxide the amount of hydroperoxide formed was less than 5%. The analysis of ring and disk currents confirms the role of transition metal

oxide as a decomposer catalyst for the hydroperoxide without a significant contribution to the primary electro-reduction of oxygen that occurs on carbon.

The synergistic function of carbon and transition metal oxide was also reported by Savinova *et al.* [5] Our studies have confirmed the mechanism by which the transition metal oxide serves to enhance oxygen reduction activity. Detailed analysis of ring and disk currents will be presented. These findings provide new insights for the design of electrocatalysts based on various carbon-containing composite transition metal oxide catalysts for promoting the oxygen reduction reaction.

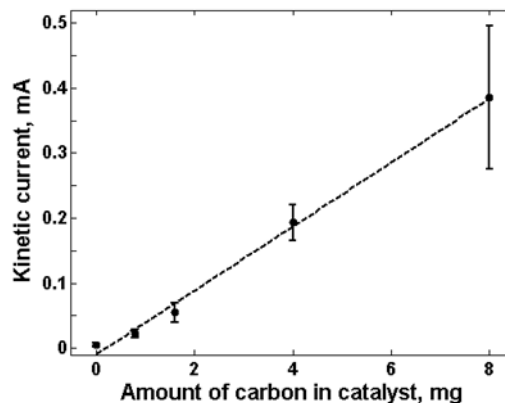


Figure 1. Kinetic current for oxygen reduction reaction at -100 mV (vs. Hg/HgO 20% KOH) in 1M potassium hydroxide saturated with oxygen for composite catalysts of varying amounts of carbon and fixed amount of LCCO (8 mg)

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